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**UNUSUAL METALLOPORPHYRINS**

**Minoru Tsutsui, et al**

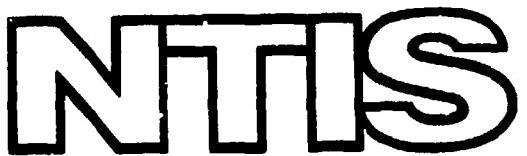
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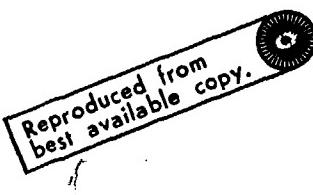


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<p>Unusual metalloporphyrins</p> <p>technetium organometalloporphyrins</p> <p>(H-MP)Tc(CO)<sub>3</sub></p> <p>mixed rhenium technetium organometalloporphyrin</p> <p>(OC)<sub>3</sub>ReMPTc(CO)<sub>3</sub></p> <p><math>\mu</math>-[meso-tetraphenylporphinato]bis[tricarbonyl-rhenium(I)]</p> <p>TPP[Re(CO)<sub>3</sub>]<sub>2</sub></p> <p>"sitting-atop complex"</p> <p>hetero-dinuclear organometalloporphyrin complexes</p> <p>monotechnetium porphyrin complex</p> <p>monocarbonyl ruthenium(II) tetraphenylporphine</p> <p>TPPRuCO</p> <p>dinitrosylruthenium(II) mesoporphyrin complex</p>						

UNUSUAL METALLOPORPHYRINS<sup>1</sup>

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Minoru Tsutsui\* and C. P. Hrung

Department of Chemistry, Texas A&M University, College  
Station, Texas 77843

The use of metal carbonyls for the insertion of metal ions into porphyrins was first introduced by Tsutsui and co-workers<sup>2,3</sup> in 1966. This method has developed itself to be a useful and unique technique in the synthesis of new metalloporphyrin complexes within the last decade. In addition to a number of previously reported metalloporphyrins, the reaction of metal carbonyls and metal carbonyl halides with neutral porphyrins has led to the syntheses of new metalloporphyrin complexes of chromium, molybdenum, technetium, ruthenium, rhodium, rhenium, and iridium.<sup>4</sup> Except for the chromium and molybdenum porphyrin complexes, carbonyl groups are retained by the metals in the new metalloporphyrin complexes.

By reaction of dirhenium decacarbonyl,  $\text{Re}_2(\text{CO})_{10}$ , or ditechnetium decacarbonyl,  $\text{Tc}_2(\text{CO})_{10}$ , with mesoporphyrin IX dimethyl ester,  $\text{H}_2\text{MPIXDME}$ , in refluxing decalin under argon, Tsutsui and coworkers have successfully prepared two unusual rhenium organometallopheophytins<sup>5,6</sup>,  $(\text{H-MP})\text{Re}(\text{CO})_3$ , I, and  $\text{MP}(\text{Re}(\text{CO}))_2$ , II, a pair of technetium organometalloporphyrins,<sup>7,8</sup>  $(\text{H-MP})\text{Tc}(\text{CO})_3$ , III, and  $\text{MP}(\text{CO})_3$ , IV, and a mixed rhenium technetium organometalloporphyrin,<sup>9</sup>  $(\text{OC})_3\text{ReMPtC}(\text{CO})_3$ , V, (Figure 1). A single crystal X-ray diffraction analysis of  $\mu$ -[meso-tetraphenylporphinato]bis[tricarbonylrhenium(I)]<sup>10</sup>, TPP[ $\text{Re}(\text{CO})_3$ ]<sub>2</sub>, VI, (Figure 2), has shown that each rhenium ion is bonded to three nitrogen atoms and that two rhenium atoms are bonded to one porphyrin on opposite sides of the plane of the porphyrin molecule.

The metal ions in these complexes, I-VI, sit out of the plane of the porphyrin molecule. The monorhenium and monotechnetium organometalloporphyrin complexes, I and III, where the porphyrin moiety acts as a tridentate ligand, resemble Fleischer's proposed "sit-

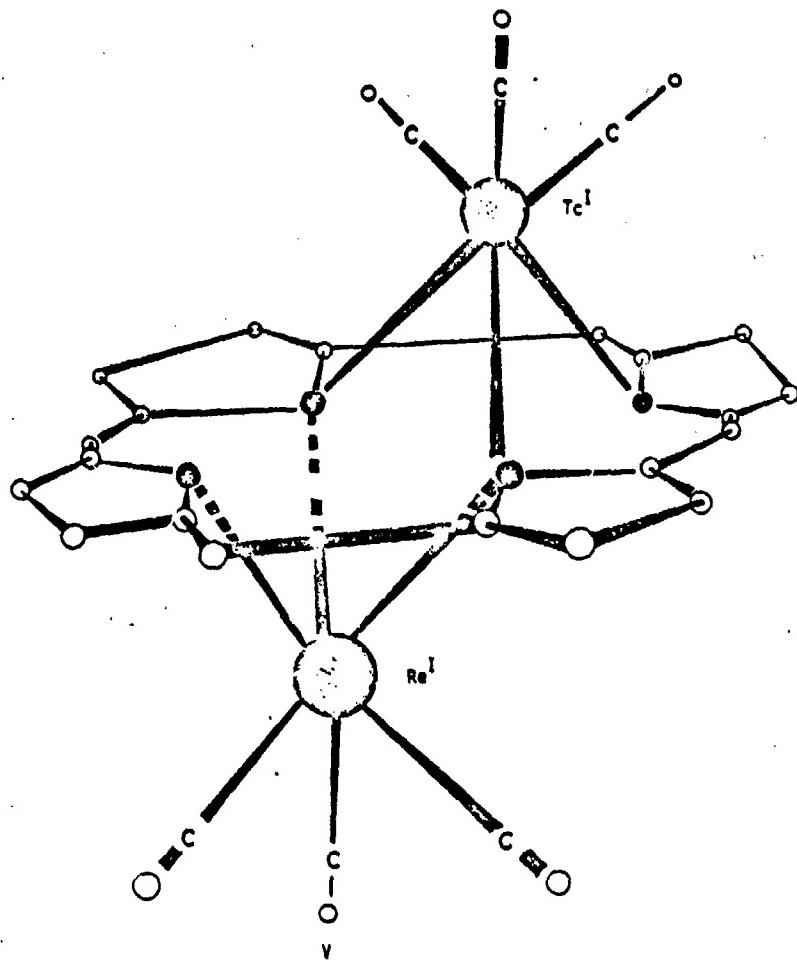


Figure 1. Schematic diagram of  $(OC)_3ReMpTc(CO)_3$ , V; The alkyl substituents on the porphyrin ring were omitted for clarity.

ting-atop complex<sup>11,12</sup> and are good models for the intermediates in the insertion of a metal ion into porphyrin.<sup>13</sup> The dirhenium, ditechnetium, and the mixed rhodium technetium organometalloporphyrin complexes, II, IV, V, and VI, where the porphyrin moiety acts as a hexadentate ligand, are examples of the first isolated stable homo- and hetero-dinuclear organometalloporphyrin complexes.<sup>9</sup> The monorhenium porphyrin complex, I, reacts with  $Re_2(CO)_{10}$  or  $Tc_2(CO)_{10}$  in refluxing decalin to form rhenium porphyrin complex,<sup>5</sup> II, and the mixed rhodium technetium porphyrin complex,<sup>9</sup> V, respectively. Replacement of the pyrrolic proton (N-H) of the monorhenium porphyrin complex by other metal ions such as  $Ag^+$ ,  $Hg^{2+}$ , and  $Pb^{2+}$ , has re-

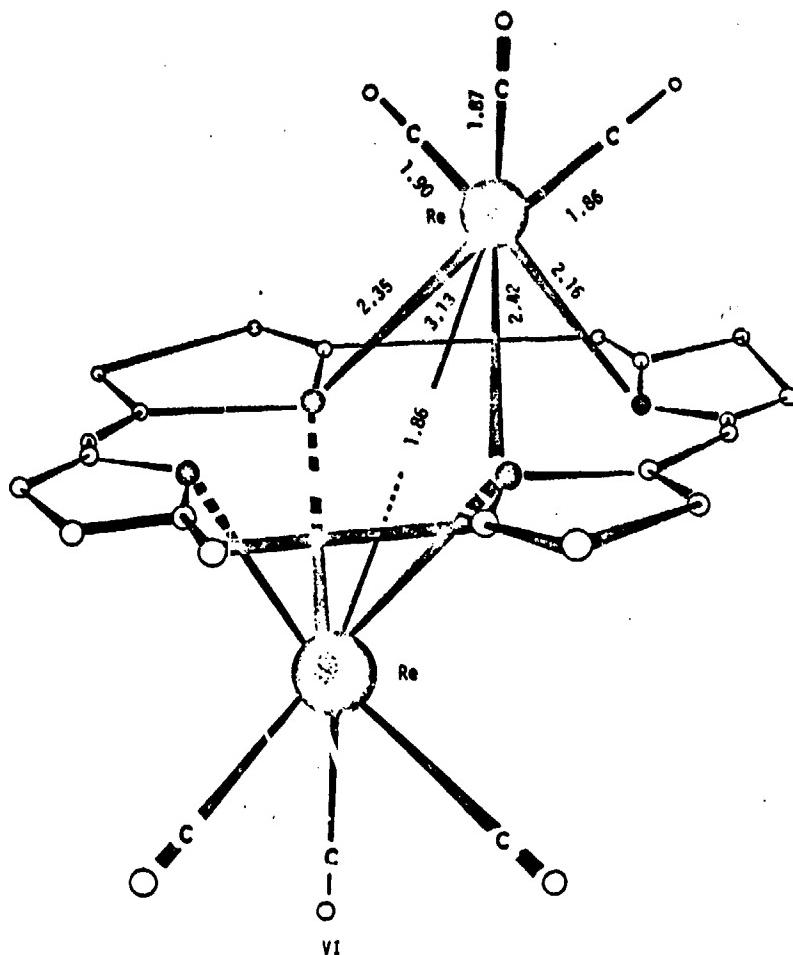


Figure 2. Coordination sphere showing bond distances around the Re atoms of  $\text{TPP}[\text{Re}(\text{CO})_3]_2$ , VI.

sulted in unstable complexes.<sup>6</sup>

The temperature dependent nmr spectra of  $(\text{HMP})\text{Tc}(\text{CO})_3$ ,  $(\text{HMP})\text{Re}(\text{CO})_3$  and  $(\text{H-TPP})\text{Re}(\text{CO})_3^{14}$  have been shown to exhibit fluxional behavior. The metal atoms migrate about the face of the porphyrin ring via an intramolecular mechanism. This is the first example of fluxional behavior of out-of-plane organometalloporphyrins reported.

The monotechnetium porphyrin complex, III, (Figure 3), behaves in a different manner by disproportionating<sup>7,8</sup> to form a ditechnetium porphyrin complex, IV, and the free porphyrin,  $\text{H}_2^{\text{MIXDME}}$ , by heating

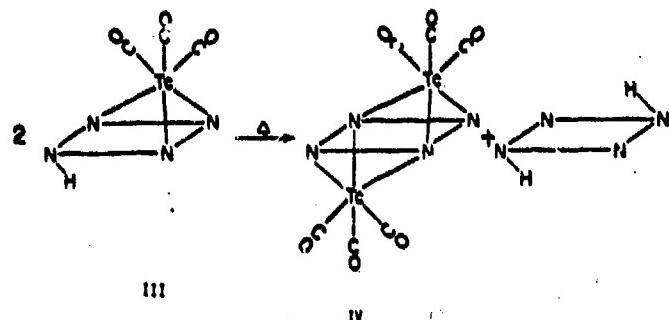


Figure 3. Disproportionation of  $(\text{H-Mp})\text{Tc}(\text{CO})_3$ , III, by heating.

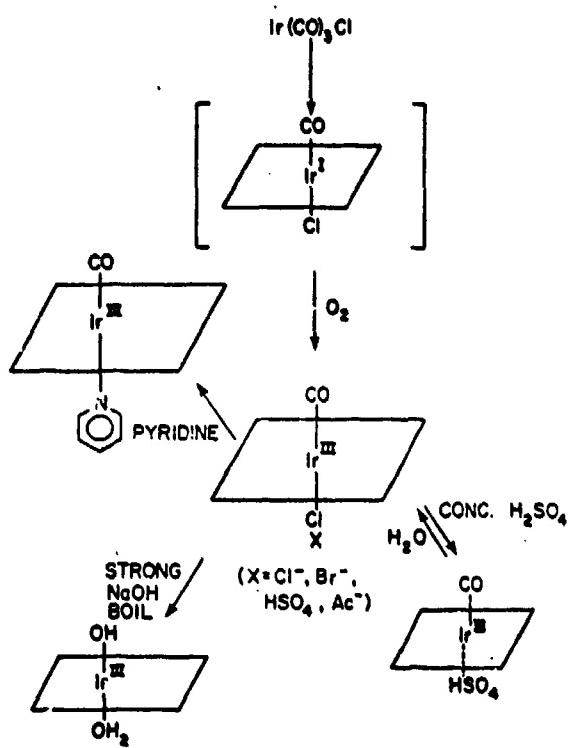


Figure 4. Reaction scheme for iridium porphyrin prepared via  $\text{Ir}(\text{CO})_3\text{Cl}$ .

in refluxing decalin<sup>8</sup> (Figure 4). This is also the first example of unusual coordination phenomenon reported. Such a reaction was not observed on heating monorhenium porphyrin complex,  $\text{I}$ , in re-

fluxing decalin.<sup>5,6</sup> It seems that both the rhenium and technetium dimetalloporphyrin complexes are thermodynamically more stable than the monometalloporphyrin complexes, because a reverse reaction of  $Mp[M(CO)_3]_2$  to  $(H-Mp)M(CO)_3$ , ( $M = Re$  or  $Tc$ ), could not be detected between  $Mp[M(CO)_3]_2$  and  $H_2MPXIDME$  in refluxing decalin for either the rhenium or technetium dimetalloporphyrin complexes.<sup>5-8</sup>

Two different methods were employed by Fleischer and co-workers in 1967 in preparing the rhodium and iridium porphyrin complexes.<sup>15, 16</sup> In one, the freshly prepared metal carbonyl halides,  $[Rh(CO)_2Cl]_2$  and  $[Ir(CO)_2Cl]$ , were allowed to react with the porphyrins in glacial acetic acid solution to form the respective metalloporphyrins (Figure 5). In the second method, the cyclooctene complexes of rhodium and iridium were found to be reactive intermediates useful in the metalloporphyrin formation (Figure 6). In both methods, incorporation of rhodium into the porphyrin was more readily achieved than was iridium. By the reaction of  $[Rh(CO)_2Cl]_2$  with meso-tetraphenylporphine, H<sub>2</sub>TPP, in refluxing benzene, two stable organometalloporphyrin derivatives of rhodium, Rh<sup>III</sup>CO(TPP)Cl and (c-phenyl)-Rh<sup>IV</sup>(TPP)·Cl, were separated by chromatography on an alumina column by Fleischer and co-workers<sup>17,18</sup> (Figure 7).

Recently, Yoshida and co-workers were able to prepare two novel dinuclear rhodium(I) organometalloporphyrin complexes<sup>19,20</sup>, VII and VIII.

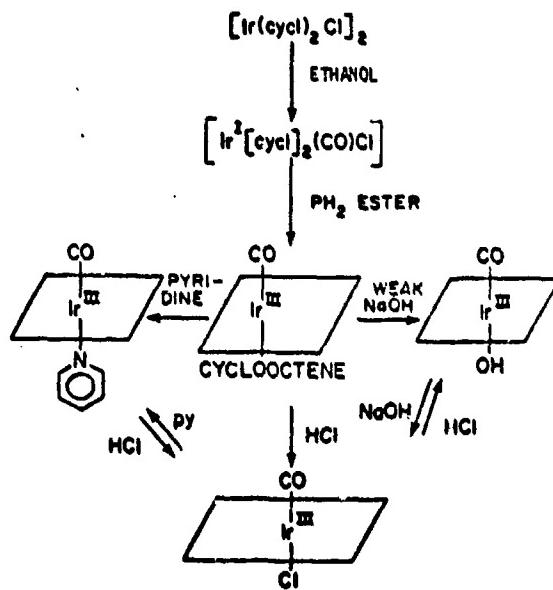


Figure 5. Reaction scheme for iridium porphyrin prepared via iridium cyclooctene complex.

VIII (figure 8), by modifying Fleischer's reaction conditions for the preparation of  $\text{Rh}^{\text{II}}\text{CO}(\text{TPP})\cdot\text{Cl}$  and  $(\sigma\text{-phenyl})\text{Rh}^{\text{IV}}(\text{TPP})\cdot\text{Cl}$  in refluxing benzene.<sup>17,18</sup> Octaethylporphyrin, OEPH<sub>2</sub>, or (*N*-methyl) octaethylporphyrin reacts with  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  in benzene solution at room temperature under nitrogen atmosphere to produce VII and VIII. From the spectral data and the experimentally determined molecular weight, VII was formulated as an acid,  $\text{H}^+[\text{OEP}\cdot\text{Rh}_2(\text{CO})_4\text{Cl}]^-$ , which

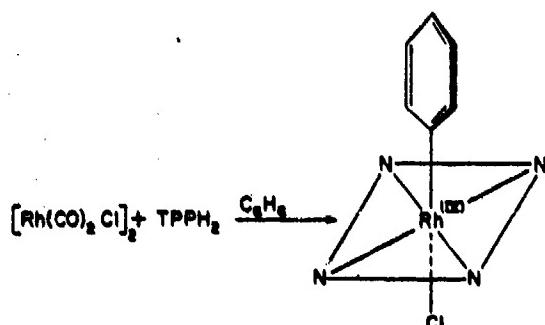


Figure 6. Preparation of new metalloporphyrin complexes of rhodium in refluxing benzene.

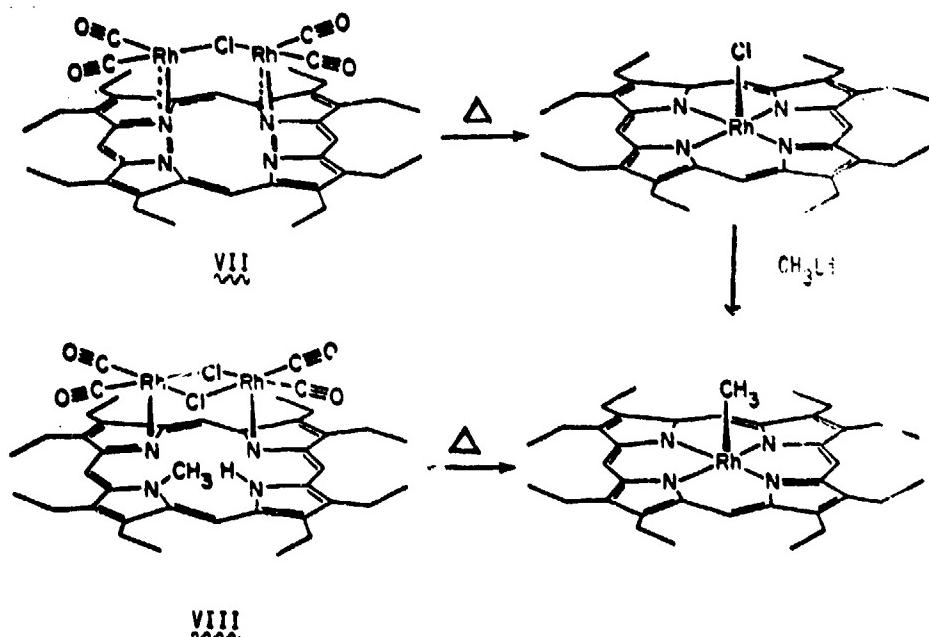


Figure 7. Two unusual metalloporphyrin complexes of rhodium prepared in benzene at room temperature.

contains a Rh-Cl-Rh bridge.<sup>20</sup> The proton nmr and infrared spectral data indicate that the  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  moiety is maintained and the N-H and N-CH<sub>3</sub> bonds exist in VIII. Since the Rh-Rh distance in  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  has been reported to be 3.12 Å, and the distance between the two adjacent nitrogen atoms of planar porphyrin is about 2.9 Å, it was assumed<sup>19</sup> that the two Rh atoms of the  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  moiety are bonded to the two adjacent nitrogen atoms of the porphyrinato core of VIII, as shown in Figure 8. X-ray analysis of VII, however, showed the atoms to lie above and below the porphyrin ring and off of the S<sub>2</sub> axis normal to the porphyrin plane (Figure 9).<sup>21</sup> Upon exposure to air, VII was slowly oxidized to form a rhodium(III) chloro complex of octaethylporphyrin,  $\text{Rh}^{\text{III}}\text{Cl}(\text{OEP}) \cdot 2\text{H}_2\text{O}$ , which can further react with alkyl lithium to give an alkyl-rhodium complex. However, VIII behaves in a different manner to give the identical alkyl-rhod-

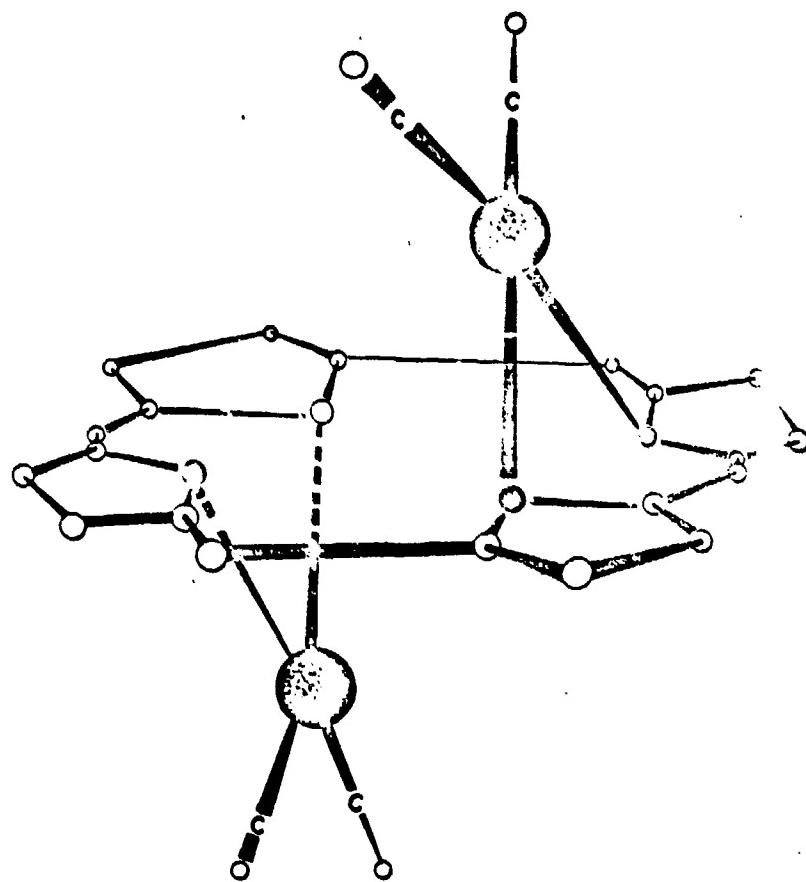


Figure 8. Structure of  $[\text{Rh}(\text{CO})_2]_2$  porphyrin.

dium complex either by gentle heating in chloroform or chromatography on silica gel (Figure 8). This phenomenon of alkyl migration from a nitrogen atom to a metal ion is reported for the first time. The alkyl migration may proceed concertedly with oxidation of rhodium(I) to rhodium(III). The N-CH<sub>3</sub> bond fission seems to be facilitated by the aid of a low-valent rhodium ion.<sup>19</sup> The reaction of (N-ethyl)octaethylporphyrin with [Rh(CO)<sub>2</sub>Cl]<sub>2</sub> yields a rhodium(I) complex similar to VIII, which is also easily oxidized to CH<sub>3</sub>CH<sub>2</sub>RhIII(OEP). The mechanism of metal oxidation and alkyl migration is still unknown.

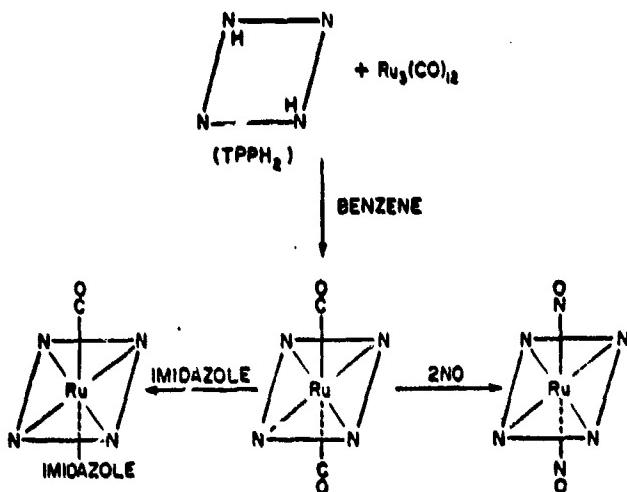


Figure 9. Reaction scheme for ruthenium(II) porphyrin.

Both ruthenium carbonyl,  $Ru_3(CO)_12$ , and ruthenium carbonyl halide,  $[Ru(CO)_2Cl]_2$ , react with tetraphenylporphine, to give the identical product, monocarbonyl ruthenium(II) tetraphenylporphine,<sup>22</sup> 23 TPPRuCO, IX. It was found that IX crystallizes with a molecule of either alcohol or water, and that these weakly bound molecules are trans to the carbonyl group.<sup>23</sup> Recently, a single crystal X-ray diffraction analysis<sup>22,24</sup> confirmed this structure. Imidazole and similar organic bases complex immediately at room temperature with TPPRuCO upon mixing in benzene.<sup>25,26</sup> However, as expected for a low-spin  $d^6$  system, substitution reactions of the monocarbonylruthenium(II) complex take place slowly and under severe conditions to replace the carbonyl group.<sup>23</sup> Irradiation of degassed benzene or pyridine solutions of monocarbonyl ruthenium(II) aetioporphyrin-I pyridinate with visible or ultra-violet light leads quantitatively to a ruthenium(II) porphyrin photodimer with a metal-metal bond.<sup>27</sup> It is of interest that MPRuCO in benzene solution reacts smoothly with excess nitric oxide to form a dinitrosylruthenium(II) mesoporphyrin complex<sup>28</sup> (Figure 10).

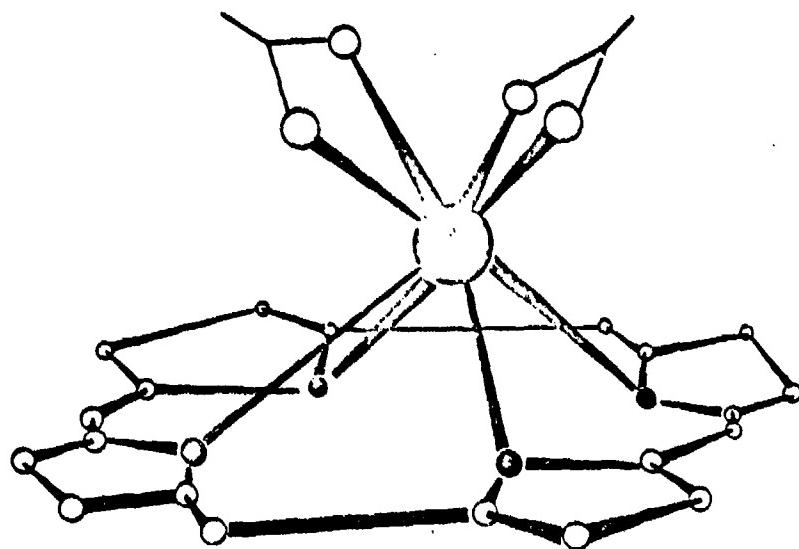


Figure 10. Scandium porphyrin.

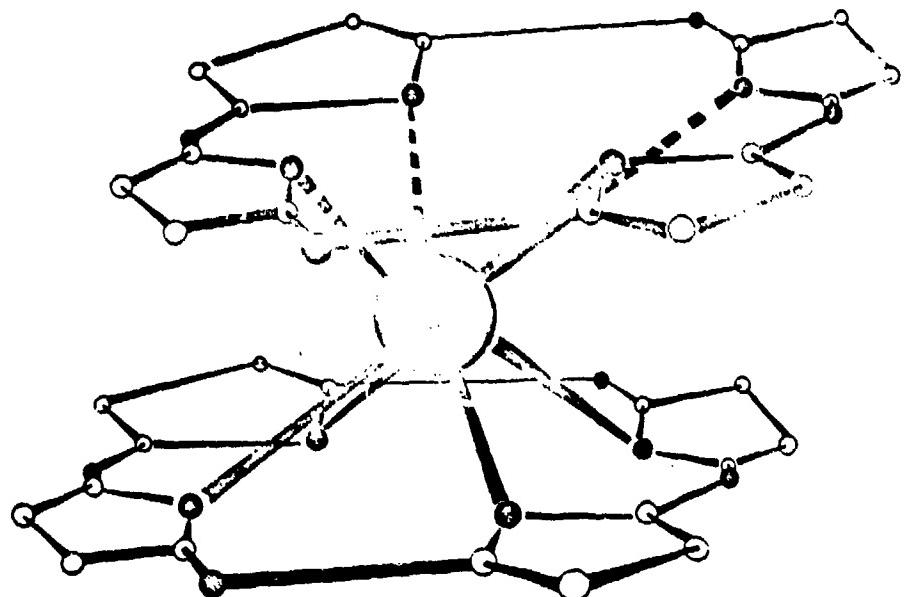


Figure 11. Structure of U(IV)bis-phthalocyanine.

From the X-ray crystal structure analysis of both rhenium and rhodium out-of-plane metalloporphyrin complexes,<sup>10,21</sup> VI and VII, it would appear that the metal carbonyl moieties prefer to coordinate to adjacent nitrogen atoms rather than alternate nitrogen atoms of the porphyrin ring, causing the metal atoms to lie off the  $S_2$  axis normal to the porphyrin plane. It is of interest that in these unusual metalloporphyrins complexes (Re, Tc, Rh), the porphyrins act as di-, tri-, or hexadentate ligands which are considered to be nonclassical coordination numbers for them. The coordination of each out-of-plane metal atom to two or three nitrogens of the porphyrin ring is predicted by the 18-electron rule with the metal in a low oxidation state (+1;  $d^6$ ,  $d^8$ ).

Further use of "unusual" synthetic metalloporphyrins is expected in elucidating the geometries which axial ligands can assume. One approach would be to examine the metalloporphyrin complexes of metals known to exhibit coordination numbers greater than six. Scandium porphyrin<sup>29,30</sup> forms complexes in which axially coordinated acetate or acetylacetate acts as a bidentate ligand. Considering the size and electronic structure of the metal and the steric requirement of the ligands, it is to be expected that the scandium is situated above the porphyrin plane. Zirconium(IV) and hafnium(IV) form porphyrin complexes<sup>29</sup> each containing two bidentate acetate ligands. It has been proposed<sup>31,32</sup> that the metal atoms are also out of the porphyrin plane, thus coordinating both acetates on the same side of the porphyrin (Figure 11).

X-ray crystal structure analysis of both uranium(IV), and tin(IV) phthalocyanine complexes<sup>33,34</sup> have shown that both complexes are sandwich type compounds with the metal atoms sitting on the  $S_2$  axis and out of the phthalocyanine plane (Figure 12). Some lanthanide(III), (La, Ce, Nd, Eu, Er, Yb) phthalocyanine complexes are also prepared and proposed to have similar sandwich structures. These out-of-plane metallic-phthalocyanine complexes are close related examples of the above reported unusual metalloporphyrins.

Recently, a "triply-decker sandwich" type polynuclear mercuric porphyrin complex<sup>36</sup> has been prepared which illustrates another type of out-of-plane metalloporphyrin complex. This compound illustrates the possibility of forming more extensive stacked polymers of metalloporphyrin (Figure 13).

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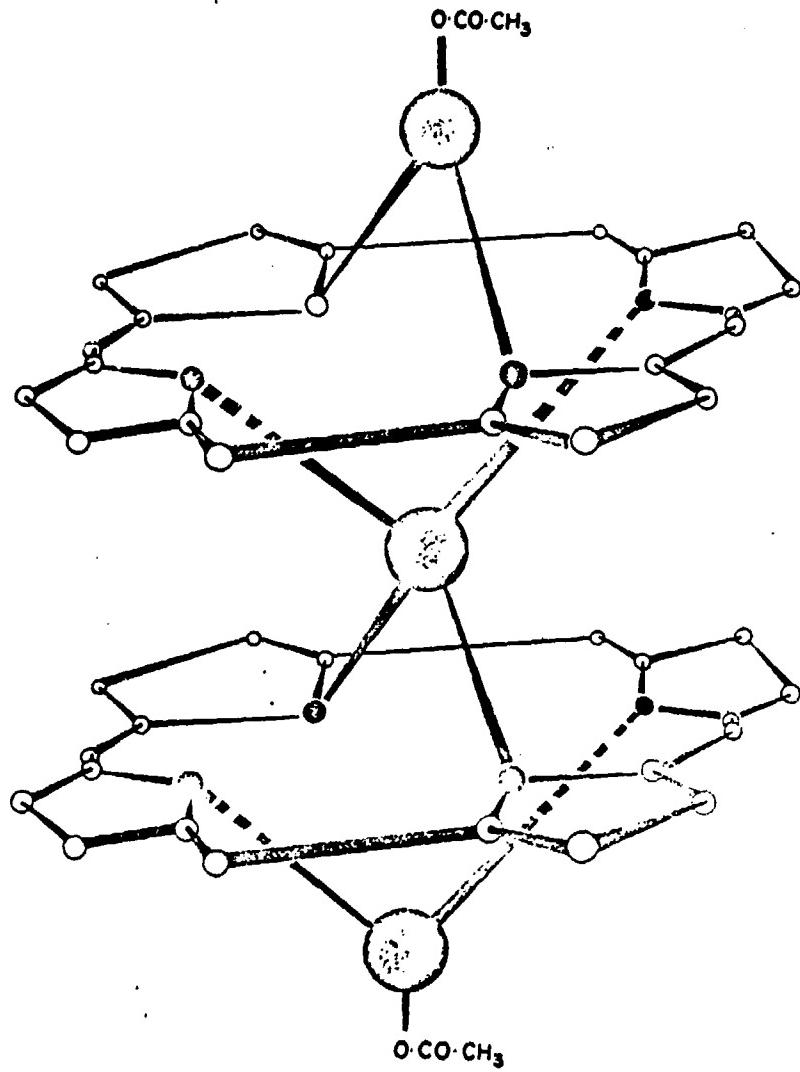


Figure 12. Proposed structure of triple decker mercury porphyrin.

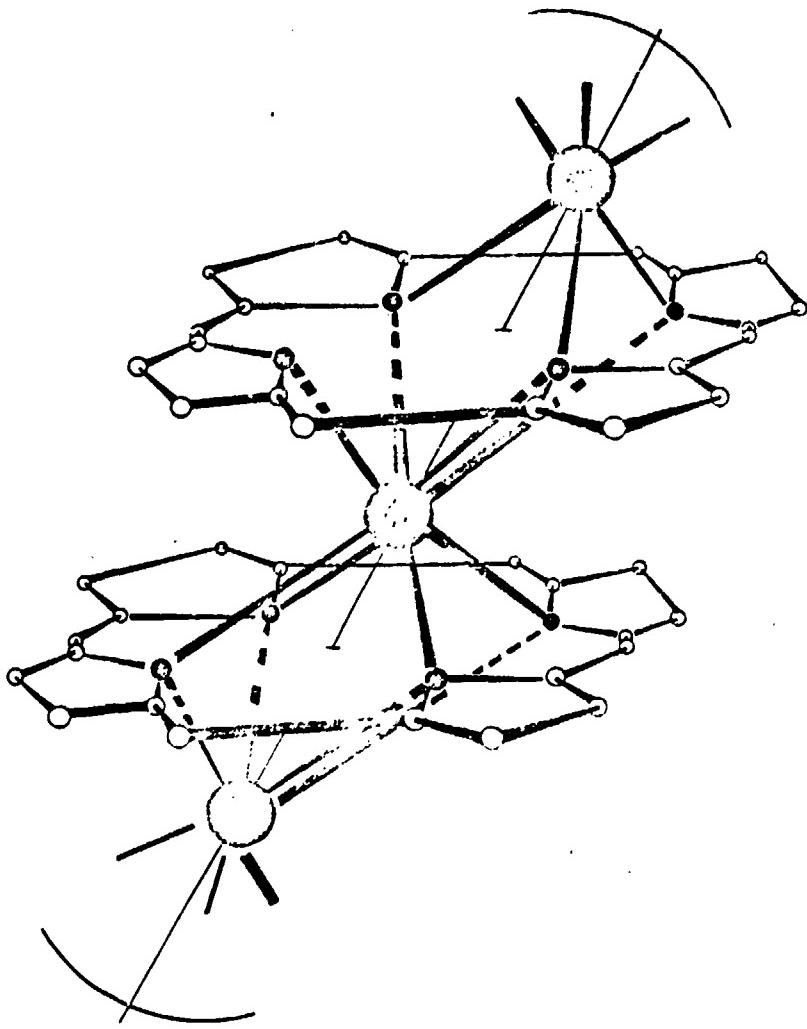


Figure 13. Proposed structure for stacked polymers of porphyrins.

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